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ELECTRICAL CONDUCTIVITY OF SINGLE CRYSTALS OF ILMENITE

A. K. MUKERJEE

DEPARTMENT OF MAGNETISM, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, JADAVPUR, CALCUTTA-32

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ABSTRACT. The electrical conductivities of the ferromagnetic single crystals of naturally occurring rhombohedral crystals of ilmenite were measured from room temperature upto 880°K for currents in the symmetry plane and in direction perpendicular to it. The study revealed that (i) the substance is a symmetric varistor with negative temperature coefficient of resistance, (ii) the non-ohmic nature of the current-voltage characteristics vanished at about 500°K; (iii) two breaks were observed in the log $_e\sigma$ $-1/T$ curve.

INTRODUCTION

Ilmenite (mainly $FeTiO_3$) is one of the chief iron and titanium bearing minerals usually found as rhombohedral crystals associated with hematite (Fe_2O_3) and magnetite (Fe_3O_4). These crystals which are very hard (H$5\frac{1}{2}-6$) have conchoidal fracture and cleavage along {0001} and {0112} (Dana 1894). These have almost iron black colour with metallic or submetallic lustre.

The magnetic properties of synthetically prepared powdered samples of ilmenite, which are only $FeTiO_3$, have been studied by some workers (Chevallier *et al.* 1953, 55; Kume 1955, Bozorth *et al.* 1957; Ishikawa and Akimoto 1958) and have been found to be antiferromagnetic but very few have (Chevallier *et al.* 1955, Bizette and Tsai 1956, Kume 1955) worked with natural crystals of ilmenite which is often known to be ferromagnetic possibly owing to the inclusion of some magnetite or a solid solution of some hematite.

The electrical conductivity, on the other hand, has been studied only by a single group of workers, namely Ishikawa and Sawada (1956) and that too with synthetic powdered samples. They worked within the temperature range of 90°K to 1073°K and observed that direct current resistivity decreased throughout this range and can according to them be represented above room temperature by the relation $\rho = \rho_0 \exp(^+E/2kT)$ where ρ is the resistivity at any temperature within the stated limit and ρ_0 and E have different values within different temperature ranges of the above limit.

On an examination of their results it is found that E, the activation energy for a particular sample, has three different values while for others only two such values.

The values of E within approximately same temperature range of two powder samples do not agree. It would appear that the samples being semiconducting, surface effects between different grains of the sample will, as is well known, be appreciable. In addition to this the directional effect of electrical conductivity cannot be observed with powders. It has therefore been decided to study the electrical conductivities of naturally occurring single crystals of ilmenite as a part of our general programme of studying the different properties of Indian minerals.

The present communication gives a preliminary report of observations on the electrical conductivities of single crystals of natural ilmenite which we obtained from the collection in this laboratory of late Prof. K. S. Krishnan.

EXPERIMENTAL

(a) *Preparation of the samples*

Before the samples are actually prepared for electrical measurements, these were examined by X-rays in order to test the reported crystal structure and also to ascertain the percentage of the ingredients of the sample, which contained somewhat more than 80% of $FeTiO_3$. Then small blocks of the specimen were fractured out from a larger single crystal by gently striking and tapping. The cleavage occurred along the *c*-plane and these blocks were ground with fine emery powder to thin rectangular tablets having the flat faces parallel to the *c*-plane. During the time of grinding the thickness was continuously checked for uniformity by a micrometer gauge.

These blocks were then electroplated with copper from a specially prepared electroplating solution. For measurement of electrical conductivity along the *c*-plane, electroplating is done over appreciable areas at the two ends on all sides of the specimen and for measurements in a perpendicular direction over two flat faces only, by coating the unwanted portions with wax.

(b) *Holders for measurement of Conductivities*

The holders for measurement of electrical conductivities along and perpendicular to the *c*-plane are in principle the same as those used by Dutta (1953) for the measurement of conductivities of graphite excepting that for *c*-plane measurements point contact was used instead of flat contact and for measurements in a perpendicular direction the glass insulating bush was replaced by syndanyo ones.

(c) *Electrical measurements*

The electrical measurements were taken in the same manner as described by Dutta (1953) and can be classified as follows.

(i) Observation of the D.C. current-voltage characteristics along *c*-plane and in perpendicular direction at room and different high temperatures produced in a cylindrical electric oven wound with nichrome wire, giving temperatures upto about 1000°C.

(ii) Measurement of the electrical conductivities along the above two directions at different high temperatures.

In addition to these, a test for detecting the presence of any rectification effect has to be made since from (i) above, the current-voltage relation has been found to be non-ohmic at room temperature. This was observed for current along both direction of the crystal. For c-plane a flat contact was placed at one end on the flat surface of the crystal which is electroplated and a copperplated tungsten whisker on the same surface at the other end. For perpendicular directions one flat surface was entirely electroplated and the whisker was placed on the other surface.

RESULTS

The result of the X-ray examination of the samples revealed that the present mineral contains more than 80% of $FeTiO_3$, the rest being magnetite and hematite.

The results of various electrical measurements at room temperature as well as higher temperatures are shown in the following Table (I) and graphs. Here $\sigma_{\parallel}$ and

TABLE I

Electrical conductivities at room temperature

Samples	Conductivity in Ω^{-1} cm^{-1}	
	$\sigma_{\parallel}$	$\sigma_{\perp}$
C_1	.38	.022
C_2	.11	.016
C_3	.20	.018

$\sigma_{\perp}$ represent the electrical conductivities along and perpendicular respectively to the c-plane.

DISCUSSION

It is observed from the results of measurements (Fig. 1-4) that at room temperature for currents passing both along and perpendicular to the c-plane, the relationship between the current passing through the crystal and the corresponding voltage drop across the specimen is non-ohmic. In view of this finding the samples were naturally tested for the presence of any rectification effect in them and it was observed that for currents along both the directions (along the plane and perpendicular to it), the current—voltage characteristic though non-ohmic in nature is

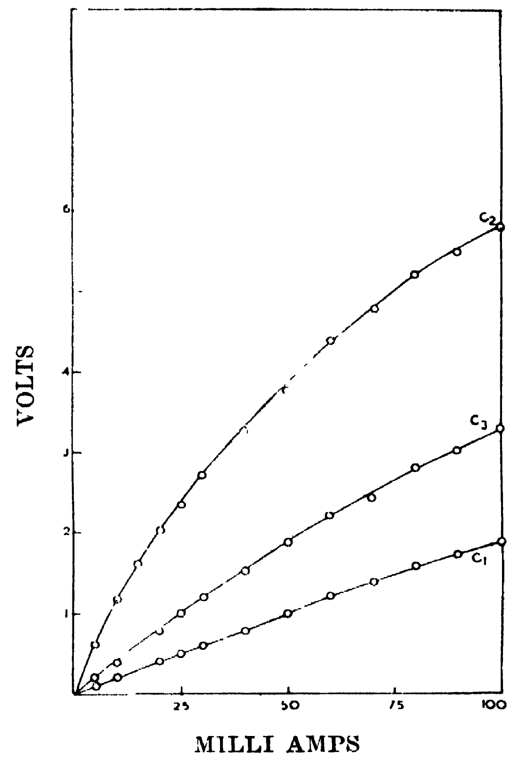


Fig. I. Current-Voltage characteristics for three crystals in the c-plane with extended contacts at both ends.

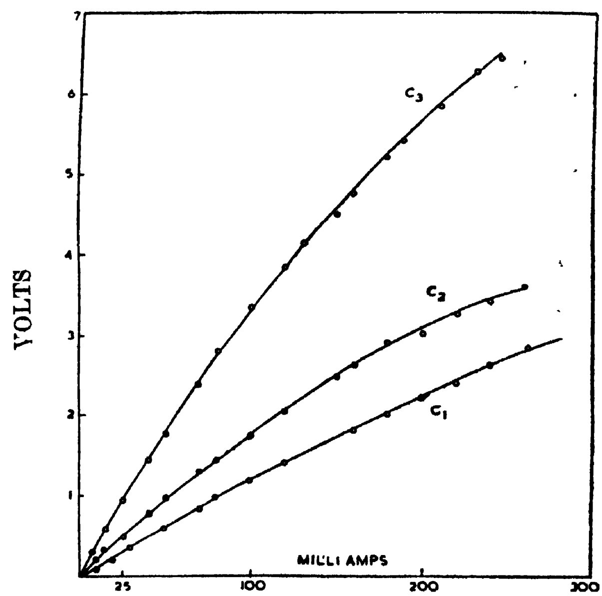


Fig. 2. Current-Voltage characteristics for three crystals perpendicular to the c-plane with extended contacts at both ends.

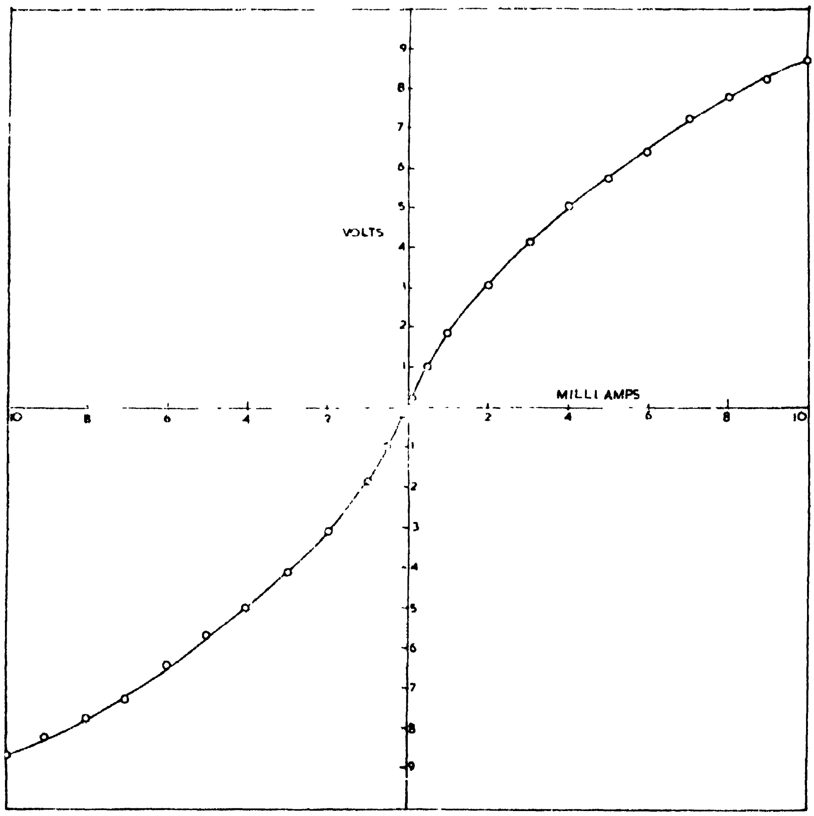


Fig. 3. Current-Voltage characteristic in the c-plane with extended contact at one end and a point contact at the other for direct and reverse currents

practically symmetrical for both forward and backward currents. Therefore the samples which will be shown subsequently to be semi-conductors are symmetrical varistors.

For finding the electrical conductivities at room temperature, the conductivities are calculated in the usual way from the linear portion of the current–voltage characteristics at very low voltage. Following this the values of $\sigma_{\parallel}$ and $\sigma_{\perp}$ have been obtained for room temperature. It is observed that the electrical anisotropy i.e. $\sigma_{\parallel}/\sigma_{\perp}$ is sufficiently large i.e. about 15.

The current-voltage characteristics reported above have been studied at different high temperatures and it was observed that the non-ohmic nature gradually decreased as the temperature was raised and ultimately vanished about 500°K and thereafter the behaviour was perfectly ohmic (see Figs. 5, 6).

The conductivities at different temperatures were obtained so long the behaviours were non-ohmic in the manner already indicated. From a study of the temperature variation of the conductivities ($\log_e \sigma$ versus $100/T$, see figs. 7, 8), it is observed that there are two distinct breaks in the curves at which both $\sigma_{\parallel}$ and $\sigma_{\perp}$ undergo

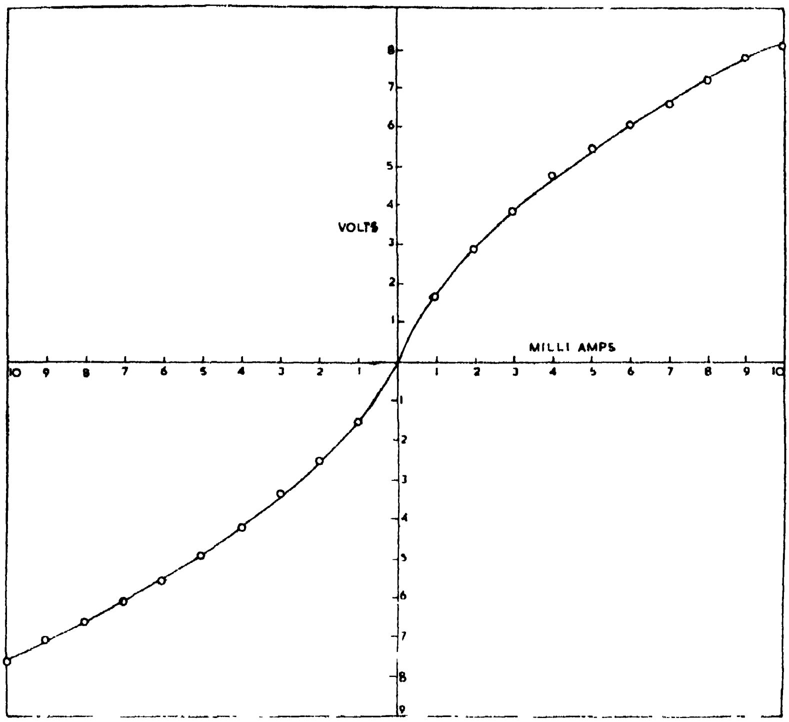


Fig. 4. Current-Voltage characteristics perpendicular to the c-plane with extended contact at one end and point contact at the other for direct and reverse currents.

very sharp changes. The temperatures are quite sharply marked and the conductivities perfectly reversible with temperature. It has been not yet possible to associate the breaks with any other physical properties. Moreover, it has been found

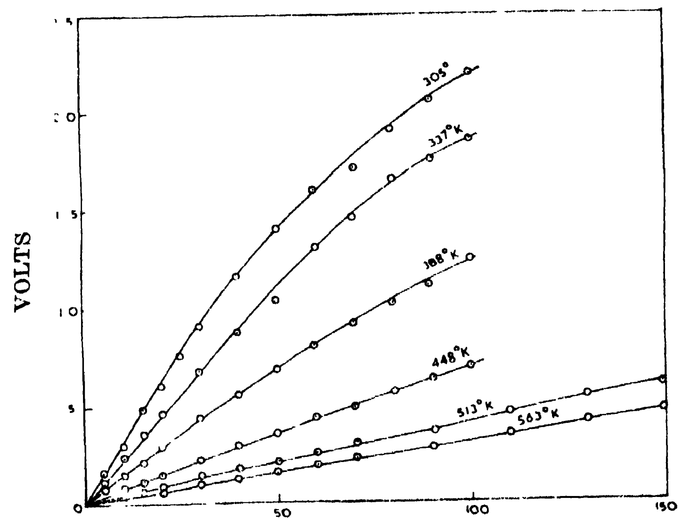


Fig. 5. Current-Voltage characteristics in c-plane at different temperatures above room temperature with extended contacts at both ends.

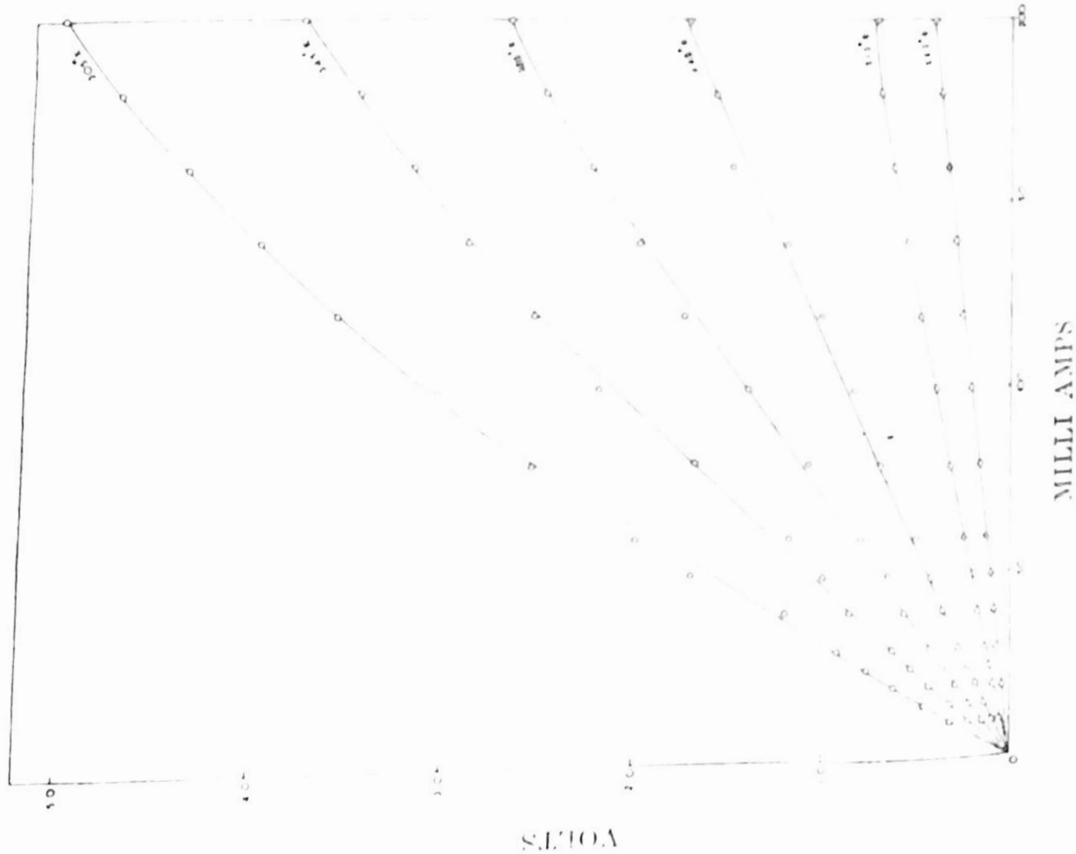
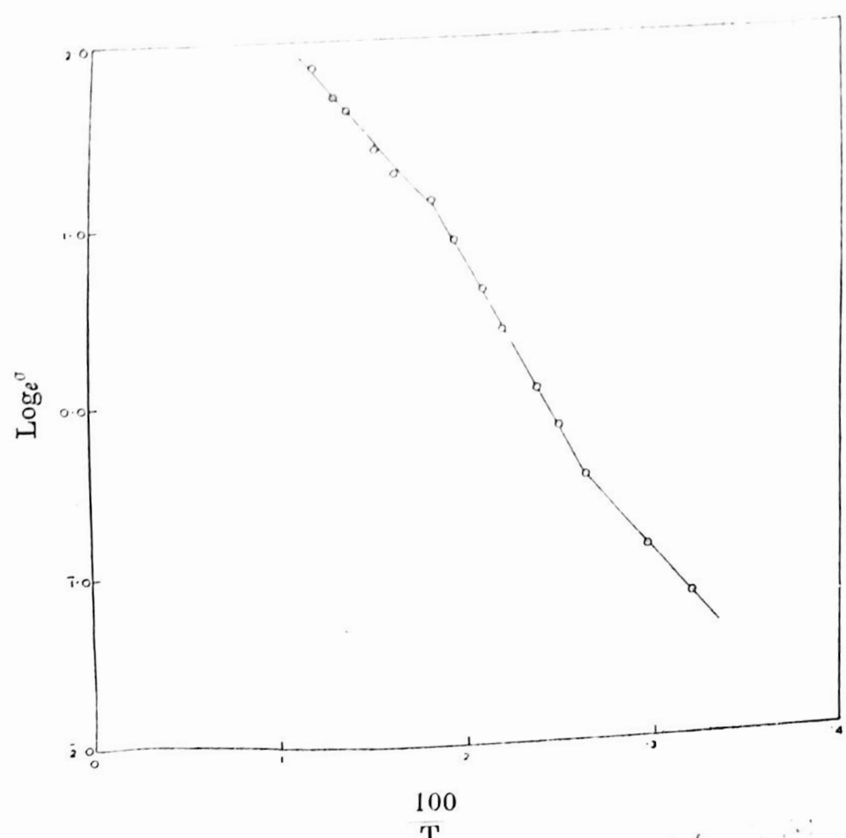


Fig. 6. Current-Voltage characteristics perpendicular to the c-plane with at different temperatures above room temperature with extended contacts at both ends



Variation of conductivity in the c-plane with temperature above room temperature.

that the breaks occur at somewhat different temperatures for directions parallel and perpendicular to the symmetry plane.

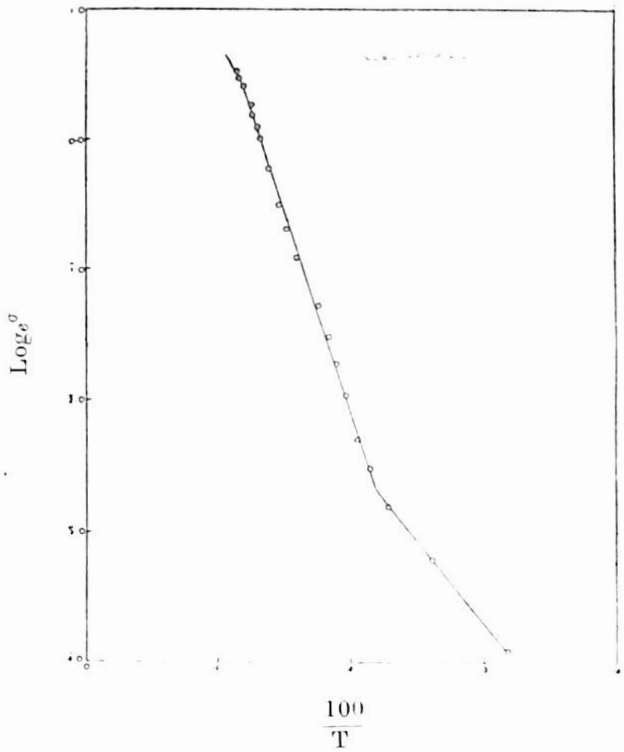


Fig. 8. Variation of conductivity perpendicular to the c-plane, with temperature above room temperature.

The temperature variation of conductivities (both $\sigma_{\parallel}$ and $\sigma_{\perp}$) can be represented by the relation

$$\sigma = Ae^{-B/T}$$

where A and B have different values for $\sigma_{\parallel}$ and $\sigma_{\perp}$ and for different temperature ranges (see Table II)

TABLE II

The values of A and B

Temperature range °K	In the plane: A in Ω^{-1} cm^{-1}	In the plane: B in °K	Temperature range °K	Perpendicular to the plane: A in Ω^{-1} cm^{-1}	Perpendicular to the plane: B in °K
305—380	16.4	1220	305—460	0.9	1250
380—556	19.5	2000	460—840	54.6	3330
556—880	24.5	1180	840—880	13.5	1860

Further measurements to explain these behaviours in the light of its structure, composition and electronic configuration are in progress, details of which will be published in due course.

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